



03/31/00

## UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.: 3797IN-1

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Express Mail Label No.: EL417666916

Title: "LUMINESCENT ORGANIC MATERIAL FOR LIGHT-EMITTING DEVICES"

Assistant Commissioner for Patents

Box Patent Application

Washington, DC 20231



Enclosed for filing with the above-identified utility patent application, please find the following:

1. ☒ Specification (Total Pages of Text, including Abstract and Claims: 12)
2. ☒ Drawing(s) (35 USC 113) (Total Sheets: 1) ☐ FORMAL ☒ INFORMAL
3. ☒ Oath or Declaration (Total Pages: 4) ☒ Signed ☐ Unsigned
4. ☒ Assignment Papers (cover sheet & document(s))
5. ☒ Return Postcard (MPEP 503) (should be specifically itemized)
6. ☒ A check in the amount of \$690.00 is enclosed.

## FEE CALCULATION:

	(COL. 1) NO. FILED				SMALL ENTITY			LARGE ENTITY	
					RATE	FEE		RATE	FEE
BASIC FEE:						\$345.00	OR		\$690.00
TOTAL CLAIMS:	8	-	20	0	X \$9 =		OR	X \$18 =	\$0.00
INDEP. CLAIMS:	3	-	3	0	X \$39 =		OR	X \$78 =	\$0.00
MULTIPLE DEPENDENT CLAIMS					+ \$130 =		OR	+\$260 =	\$0.00
*IF THE DIFFERENCE IN COL. 2 IS LESS THAN ZERO, ENTER "0" IN COL. 2.					TOTAL:				\$690.00

## OTHER INFORMATION:

1. ☒ The Commissioner is hereby authorized to debit any underpayments or credit any overpayment to Deposit Account No. 19-1970.
2. ☒ The Commissioner is hereby authorized to charge all required fees for extensions of time under §1.17 to Deposit Account No. 19-1970.
3. ☒ Foreign Priority benefits are claimed under 35 USC §119 of Italian Patent Application Serial No. BA99A 000010 filed April 1, 1999

4. Correspondence Address:

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Respectfully Submitted,

SHERIDAN ROSS P.C.

Joseph E. Kovarik  
Registration No. 33,005

Date:

3/31/00

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**TITLE OF THE INVENTION:**

LUMINESCENT ORGANIC MATERIAL FOR LIGHT-EMITTING DEVICES

5           The present invention relates to a luminescent organic material for light-emitting devices, in particular, organic LEDs.

**BACKGROUND OF THE INVENTION**

10           The luminescent organic materials, such as PPV and Alq3, currently used for making thin films in light-emitting devices, such as light-emitting diodes or LEDs, have numerous drawbacks.

15           These are normally solved by encapsulating the materials and inserting metal contacts embedded in the films.

          Moreover, the quantum efficiency and emission wavelength tunability of known materials are poor.

20           Research is therefore being conducted into materials enabling organic LEDs to be made entirely of plastic material.

**SUMMARY OF THE INVENTION**

25           It is therefore an object of the present invention to provide light-emitting devices, in particular, LEDs, designed to eliminate the aforementioned drawbacks, and which, in particular, make encapsulation and the insertion of metal contacts superfluous, enable LEDs to

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be made of organic material and using the same class of material for all the emission wavelengths in the visible spectrum, are more reliable, and are easier to produce.

According to the present invention, there is provided a luminescent material for light-emitting devices, comprising at least one thienyl-S,S-dioxide unit.

#### BRIEF DESCRIPTION OF THE DRAWING

The present invention is described in detail below, with reference also to the accompanying drawing showing a view in perspective of an organic LED in accordance with the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Number 1 in Figure 1 indicates as a whole an organic LED comprising a support 2, for instance a plastic foil, a film 3 on a side of the support 2 and respective power supplying elements; the film 3 is made of a material containing at least one thienyl-S,S-dioxide unit and directly incorporates the elements 3, without the necessity of contacting and welding; if the film 3 is self-supporting, the support 2 may be avoided.

It is well known that thiophene based materials may be selectively oxidised at the thienyl sulfurs to the corresponding thiophene-S,S-dioxides by reactions already described in the literature and therefore not reported in details.

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Thiophene-based molecules can be properly engineered by controlling the length of the chain and by inserting some functional groups, in order to tune the HOMO-LUMO gap from the blue to the red, resulting in the unprecedentedly wide tunability of the emitted light.

It has been surprisingly found that thienyl-S,S-dioxide based materials have an high quantum efficiency and also the following properties: wide spectral tunability, no degradation in time (thus avoiding the requirement of encapsulation), completely plastic device (no metal contacts) suitable for technologies over plastic substrates.

Thienyl-S,S-dioxide materials may therefore be used in thin films useful in organic light emitters.

Thienyl-S,S-dioxide materials show the highest photoluminescence efficiency ever measured for thiophene based materials in the solid state. The obtained values (mainly > 37%) are even higher than that of the organic luminescent materials which are currently under investigation for application in organic electroluminescent devices.

Main features of the thienyl-S,S-dioxide materials according to the present invention are the functionalization of the thienyl sulfur with oxygen atoms (in order to modify the HOMO and LUMO energies and

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to facilitate charge injection), which is carried out such as the material comprises at least one thiophene ring in the  $\alpha$  position of the ring of said thienyl-S,S-dioxide and grafting some alkyl substituents in the  $\beta$  position of the ring of said thienyl-S,S-dioxide to prevent the formation of planar or partly planar structures (in order to avoid  $\pi,\pi$  stacking), leading to unprecedentedly efficient photoluminescence.

The insertion of one non-aromatic thienyl-S,S-dioxide unit within the skeleton of an oligothiophene does not modify the  $\pi,\pi^*$  character of the frontier orbitals but decreases their energy and that of the LUMO more than that of the HOMO.

The oligomers containing a thienyl-S,S-dioxide moiety are characterized by much greater electron affinities and slightly higher oxidation potentials than their 'fully aromatic' counterparts. This results in a substantial enhancement of the electron injection capability of the compound, with strong impact on the electrical performance of the device.

Furthermore, the oxygen atoms modify the self organization properties of the molecules in the solid state. Indeed, the molecular packing of these new molecules is characterized by the presence of a number of extremely short van der Waals separations, all

- 5 -

involving the oxygen atoms. The peculiar molecular packing causes a strong enhancement of the quantum efficiency of the thiophene solid films.

5 In conclusion, thienyl-S,S-dioxide based materials allow to achieve all the modifications needed to optimize the electronic properties and the solid state morphology of thiophenes required for LED applications.

10 The advantages of the luminescent material according to the present invention will be clear from the foregoing description.

15 In this way one can envisage the application of a new generation of solid state thiophene films for high-efficiency, colour-tunable LEDs operating with reduced currents and without relevant problems of chemical stability.

In particular, the luminescent material used in the organic LED according to the present invention provides for wide tunability of the energy emitted, from blue to infrared, and high quantum efficiency.

20 Moreover, functionalizing the sulfur in the thiophene ring with oxygen atoms provides for increasing the electron affinity of the molecule to ensure improved electron injection; increasing ionization potential to make the molecule more stable with respect to water and  
25 oxygen; modulating HOMO and LUMO energies and the HOMO-LUMO energy gap by appropriately alternating modified

Moreover, inserting a thiophene ring functionalized with oxygen atoms in oligothiophenes of appropriate length and symmetry provides for maintaining or increasing intrinsic quantum efficiency and for modulating the wavelength of the emitted light.

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### Example 1

### Comparative table

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TABLE 1



- 7 -

	Quantum Efficiency	Electrical Conductivity	Degradation	Processing	Tunability
Thiophenes	Low	Good	No	Easy	Yes
PPV	High	Low	Yes	Encapsulation + contacts	Weak
Al (q3)	High	Low	Weak	Encapsulation + contacts	No

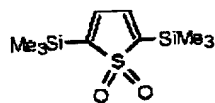
## Example 2

In table 2 are reported molecular structure, fluorescence frequencies and efficiency of selected oligothiophene-S,S-dioxides which have been obtained according to the present invention, operating in conventional manner the necessary chemical reactions, which are accordingly not reported.

10 TABLE 2

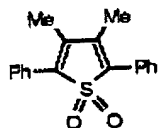
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Sample Molecular Structure       $\eta$  (%)       $\lambda_{PL}$  (nm)



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405



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470

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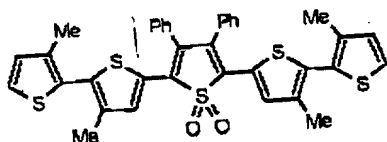
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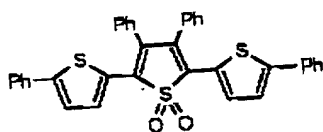
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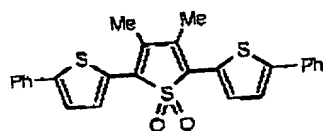
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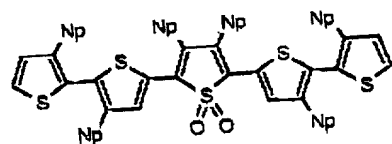


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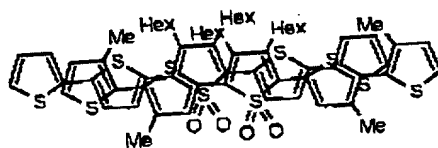


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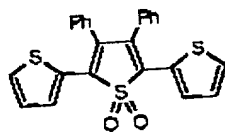
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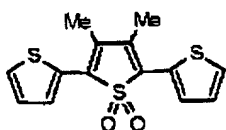


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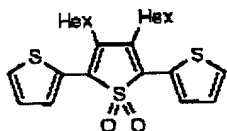
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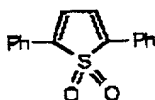
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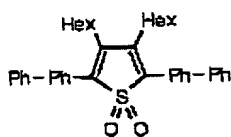
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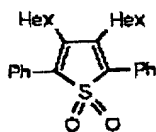
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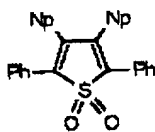
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wherein Me = methyl; Hex = n-hexyl; Np = neo-pentyl;  
 Ph = phenyl; Ph-Ph = p-biphenyl.

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## CLAIMS

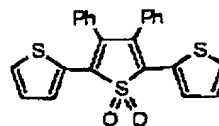
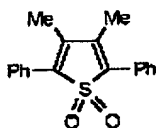
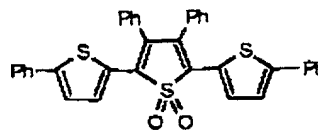
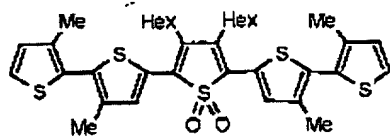
1) A luminescent organic material for light-emitting devices, characterized by comprising at least one thienyl-S,S-dioxide unit.

2) A luminescent organic material as claimed in Claim 1, characterized by comprising at least one thiophene ring in the  $\alpha$  position of the ring of said thienyl-S,S-dioxide.

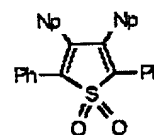
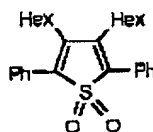
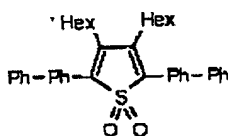
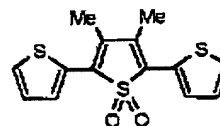
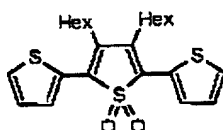
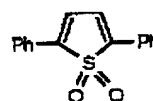
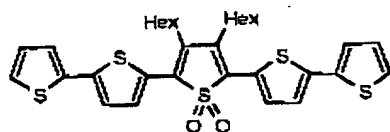
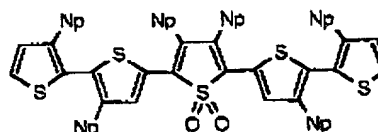
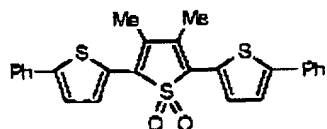
3) A luminescent organic material as claimed in Claim 2, characterized by having at least one alkyl or aryl substituent in the  $\beta$  position of the ring of said thienyl-S,S-dioxide.

4) A luminescent organic material as claimed in Claim 3, characterized in that said alkyl substituents are of such a form as to prevent  $\pi$ - $\pi$  stacking and the formation of planar or partly planar structures.

5) A luminescent organic material for light-emitting devices, characterized by comprising at least one substance selected from the group consisting of :



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wherein Me = methyl; Hex = n-hexyl; Np = neo-pentyl; Ph = phenyl; Ph-Ph = p-biphenyl

6) Use of a luminescent material as claimed in Claim 1 in contacts.

7) Use of a luminescent material as claimed in Claim 1 in organic LEDs.

8) A light-emitting diode comprising a luminescent material, characterized in that said luminescent material comprises at least a thienyl-S,S-dioxide.

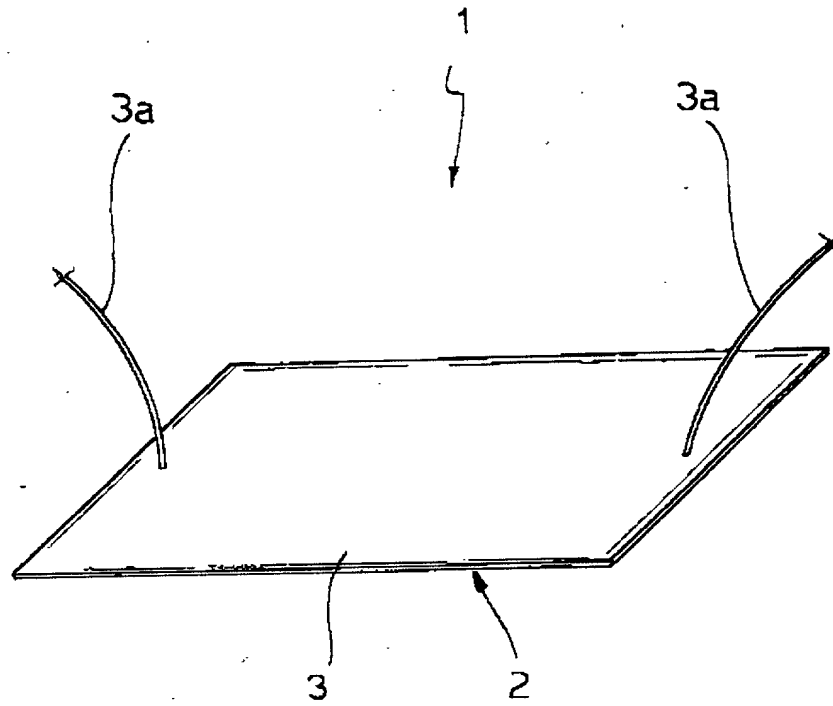
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## ABSTRACT

A luminescent organic material for light-emitting devices, in particular, for organic LEDs, having at least one thienyl-S,S-dioxide unit obtained by functionalizing the sulfur of a thiophene ring. Inserting a thiophene ring functionalized with oxygen atoms in oligothiophenes of appropriate length and symmetry provides for maintaining or increasing intrinsic quantum efficiency and for modulating the wavelength of the emitted light.

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# Declaration and Power of Attorney For Patent Application

## Modulo di Dichiarazione Per Domanda di Brevetto

### Italian Language Declaration

Io, sottoscritto inventore, dichiaro con il presente che:

Il mio domicilio, recapito postale e cittadinanza sono quelli indicati in calce accanto al mio nome,

Che mi reputo in buona fede essere l'inventore originario, primo e unico (qualora un solo nominativo appaia elencato appresso) o il coinventore (qualora i nominativi siano piu' di uno) primo e originario dell'invenzione da me rivendicata, e per la quale faccio domanda di brevetto. Tale invenzione é chiamata

e la sua descrizione é:

☐ qui acclusa.

☐ E' stata presentata il \_\_\_\_\_ as

Come Domanda Numero \_\_\_\_\_

ed e' stata rettificata il \_\_\_\_\_  
(se applicabile)

Dichiaro inoltre con il presente di aver letto e compreso il contenuto della specificazione sopra indicata, comprese le rivendicazioni, come rettificata da qualsiasi emendamento a cui si sia accennato sopra.

Riconosco il mio dovere di rivelare informazioni che costituiscano materiale per l'esame della presente domanda secondo i termini del Titolo 37, Codice dei Regolamenti Federali, Comma 1,56(a).

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"LUMINESCENT ORGANIC MATERIAL FOR

LIGHT-EMITTING DEVICES"

the specification of which

☒ is attached hereto

☐ was filed on \_\_\_\_\_

as Application No. \_\_\_\_\_

and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability and examination of this application in accordance with Title 37, Code of Federal Regulations, 51.56(a).



## Italian Language Declaration

Con il presente rivendico i benefici di priorità per l'estero come stabilito dal Titolo 35, Codice degli Stati Uniti, Comma 119, per qualsiasi domanda di brevetto (o brevetti) straniera o per qualsiasi certificato d'invenzione sotto elencato, ed ho anche elencato qui sotto tutte le domande di brevetto e certificati d'invenzione stranieri aventi una data di presentazione anteriore a quella della domanda per la quale si rivendica la precedenza:

Prior foreign applications

Domande dall'estero precedenti

BA99A000010

Italy

01.04.1999

(Number)  
(Numero)

(Country)  
(Paese)

(Day/Month/Year Filed)  
(Giorno, Mese de Anno di Presentazione)

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(Day/Month/Year Filed)  
(Giorno, Mese de Anno di Presentazione)

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(Giorno, Mese de Anno di Presentazione)

(Number)  
(Numero)

(Country)  
(Paese)

(Day/Month/Year Filed)  
(Giorno, Mese de Anno di Presentazione)

Con il presente rivendico il beneficio previsto dal Titolo 35, Codice degli Stati Uniti, Comma 120, per qualsiasi domanda (o domande) di brevetto sotto indicata, ed entro i limiti nei quali il materiale indicato in ciascuna delle domande di brevetto non è stato rivelato nella precedente domanda di brevetto americana nel modo previsto dal primo paragrafo del titolo 35, Codice degli Stati Uniti, Comma 112, riconosco il mio dovere di rivelare il materiale d'informazione, così come viene definito nel Titolo 37, Codice dei Regolamenti Federali, Comma 1.56(a), che possa essere venuto ad aggiungersi nel periodo intercorso tra la data di presentazione della domanda precedente e la data nazionale o internazionale PCT di presentazione di questa domanda:

(Application Serial No.)  
(Numero di serie della  
Domanda di Brevetto)

(Filing Date)  
(Data di  
presentazione)

(Stato Giuridico)  
(Brevetto, in attesa  
di Brevetto, Abbandonato)

(Status)  
(patented, pending,  
abandoned)

(Application Serial No.)  
(Numero di serie della  
Domanda di Brevetto)

(Filing Date)  
(Data di  
presentazione)

(Stato Giuridico)  
(Brevettato, in attesa  
di Brevetto, Abbandonato)

(Status)  
(patented, pending,  
abandoned)

Dichiaro inoltre con il presente che tutte le informazioni da me fornite sono in fede mia vere, e che tutte le affermazioni da me fatte sono in fede mia vere; dichiaro inoltre che quando ho fatto queste affermazioni ero al corrente del fatto che false dichiarazioni fatte intenzionalmente sono punibili con multa o incarcerazione, o ambedue, secondo quanto stabilito dalla sezione 1001 del Titolo 18 del Codice degli Stati Uniti, e che tali informazioni intenzionalmente false possono mettere a repentaglio la validità della domanda o brevetto rilasciata in base ad esse.

I hereby claim foreign priority benefits under Title 35, United States Code, §119, of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Priority claimed

Priorità Rivendicata

☒  
Yes  
Sì

☐  
No  
No

☐  
Yes  
Sì

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No  
No

☐  
Yes  
Sì

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No  
No

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Yes  
Sì

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No  
No

I hereby claim the benefit under Title 35, United States Code, §120, of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a), which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## Italian Language Declaration

**PROCURA:** Io, sottoscritto inventore, nomino con la presente il seguente Procuratore (o Procuratori) o Agente (Agenti) che s'incarica di perseguire questa pratica e di portare a termine tutte le operazioni necessarie all'Ufficio Brevetti e all'Ufficio Marchi di Fabbrica pertinenti a questa pratica. (Elencare il Nome e il Numero di Matricola):

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (*list name and registration number*)

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1700 Lincoln Street - 3500 Suite  
DENVER, COLORADO 80203

Telefonare a: (Nome e Numero)

Direct Telephone Calls to: (name and telephone number)

(303) 863 9700

Nome Completo dell'inventore primo e unico		Full name of sole or first inventor <b>Giovanna BARBARELLA</b>	
Firma dell'inventore	Data	Inventor's signature <i>G. Barbarella</i>	Date March 22, 2000
Residenza		Residence c/o CNR - I.CO.C.E.A. (Bologna) (Italy)	
Cittadinanza		Citizenship Italian	
Recapito o Casella Postale		Post Office Address c/o CNR - I.CO.C.E.A. Via Gobetti 101 - 40129 Bologna Italy	
Nome completo del secondo coinventore se applicabile		Full name of second joint inventor, if any <b>Laura FAVARETTO</b>	
Firma del secondo inventore	Data	Second Inventor's signature <i>Laura Favaretto</i>	Date March 22, 2000
Residenza		Residence c/o CNR - I.CO.C.E.A. - BOLOGNA (Italy)	
Cittadinanza		Citizenship ITALIAN	
Recapito o Casella Postale		Post Office Address c/o CNR - I.CO.C.E.A. Via GOBETTI 101 40129 BOLOGNA (Italy)	

(Si prega di fornire stesse informazioni e firme di eventuali terzi e più' coinventori.)

(Supply similar information and signature for third and subsequent joint inventors.)

Nome completo del terzo coinventore se applicabile		Full name of third joint inventor, if any <b>Massimo ZAMBIANCHI</b>	
Firma del terzo inventore	Date	Third Inventor's signature <i>Massimo Zambianchi</i>	Date March 22, 2000
Residenza		Residence c/o <i>Flora CNR</i> - Bologna (Italy)	
Cittadinanza		Citizenship <i>Italian</i>	
Recapito o Casella Postale		Post Office Address c/o CNR - I.CO.C.E.A. <i>Via Gobetti 101 - 40129 BOLOGNA (Italy)</i>	
Nome completo del quarto coinventore se applicabile		Full name of fourth joint inventor, if any <b>Roberto CINGOLANI</b>	
Firma del quarto inventore	Date	Fourth Inventor's signature <i>R. Cingolani</i>	Date March 22, 2000
Residenza		Residence c/o UNIVERSITY OF LECCE - LECCE (Italy)	
Cittadinanza		Citizenship <i>ITALIAN</i>	
Recapito o Casella Postale		Post Office Address c/o UNIVERSITA' DI LECCE <i>VIA ARNESANO 73100 LECCE (Italy)</i>	
Nome completo del quinto coinventore se applicabile		Full name of fifth joint inventor, if any <b>Giuseppe GIGLI</b>	
Firma del quinto inventore	Date	Fifth Inventor's signature <i>Giuseppe Gagli</i>	Date March 22, 2000
Residenza		Residence c/o UNIVERSITA' DI LECCE - LECCE (Italy)	
Cittadinanza		Citizenship <i>ITALIAN</i>	
Recapito o Casella Postale		Post Office Address c/o UNIVERSITA' DI LECCE <i>VIA ARNESANO 73100 LECCE (Italy)</i>	
Nome completo del sesto coinventore se applicabile		Full name of sixth joint inventor, if any	
Firma del sesto inventore	Date	Sixth Inventor's signature	Date
Residenza		Residence	
Cittadinanza		Citizenship	
Recapito o Casella Postale		Post Office Address	
Nome completo del settimo coinventore se applicabile		Full name of seventh joint inventor, if any	
Firma del settimo inventore	Date	Seventh Inventor's signature	Date
Residenza		Residence	
Cittadinanza		Citizenship	
Recapito o Casella Postale		Post Office Address	